

# Fundamentals in Selective Catalytic Reduction (SCR), Filter, and Protocol

**Yong Wang (P.I.), Feng Gao,  
Konstantin Khivantsev,  
Ken Rappe, Mark Stewart, Janos Szanyi,**

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ACE023

**BATTELLE**

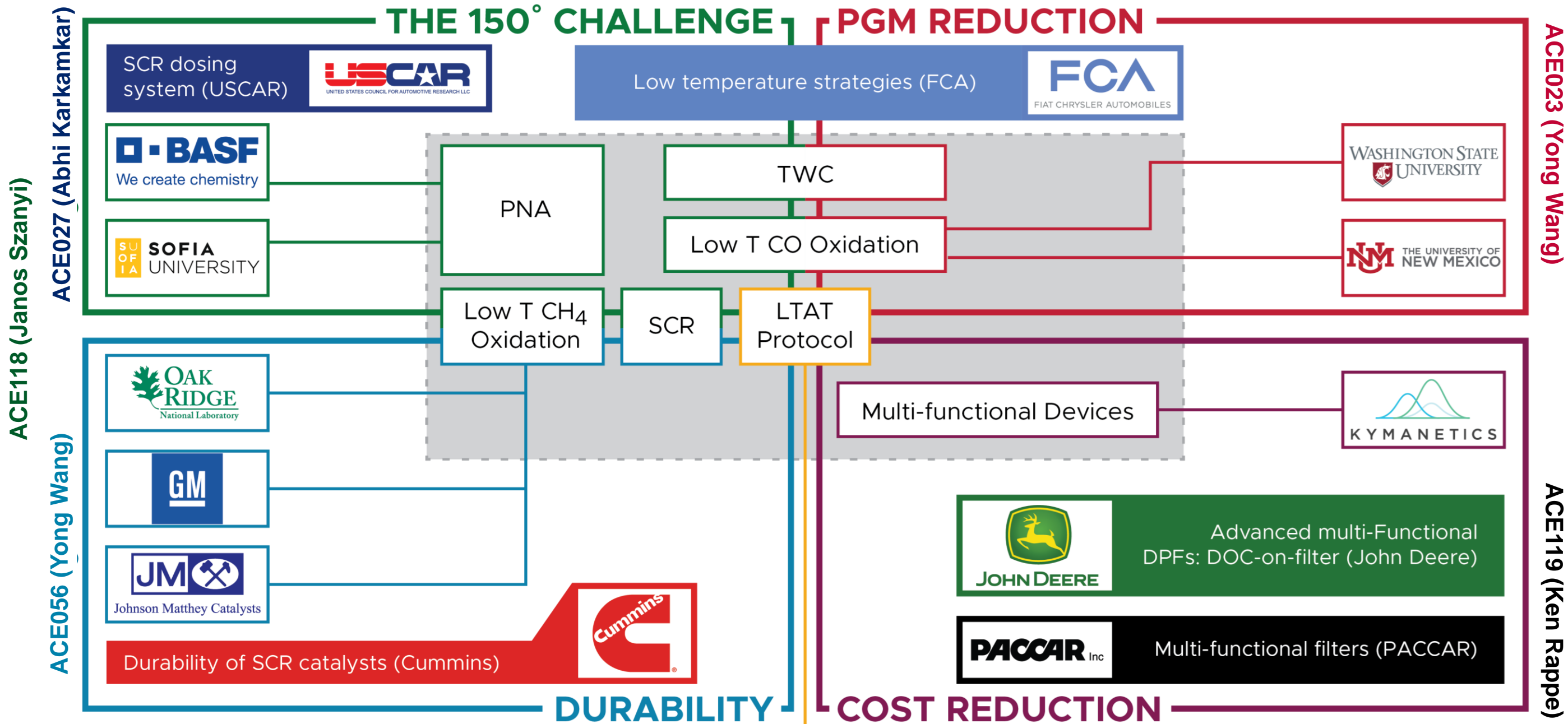
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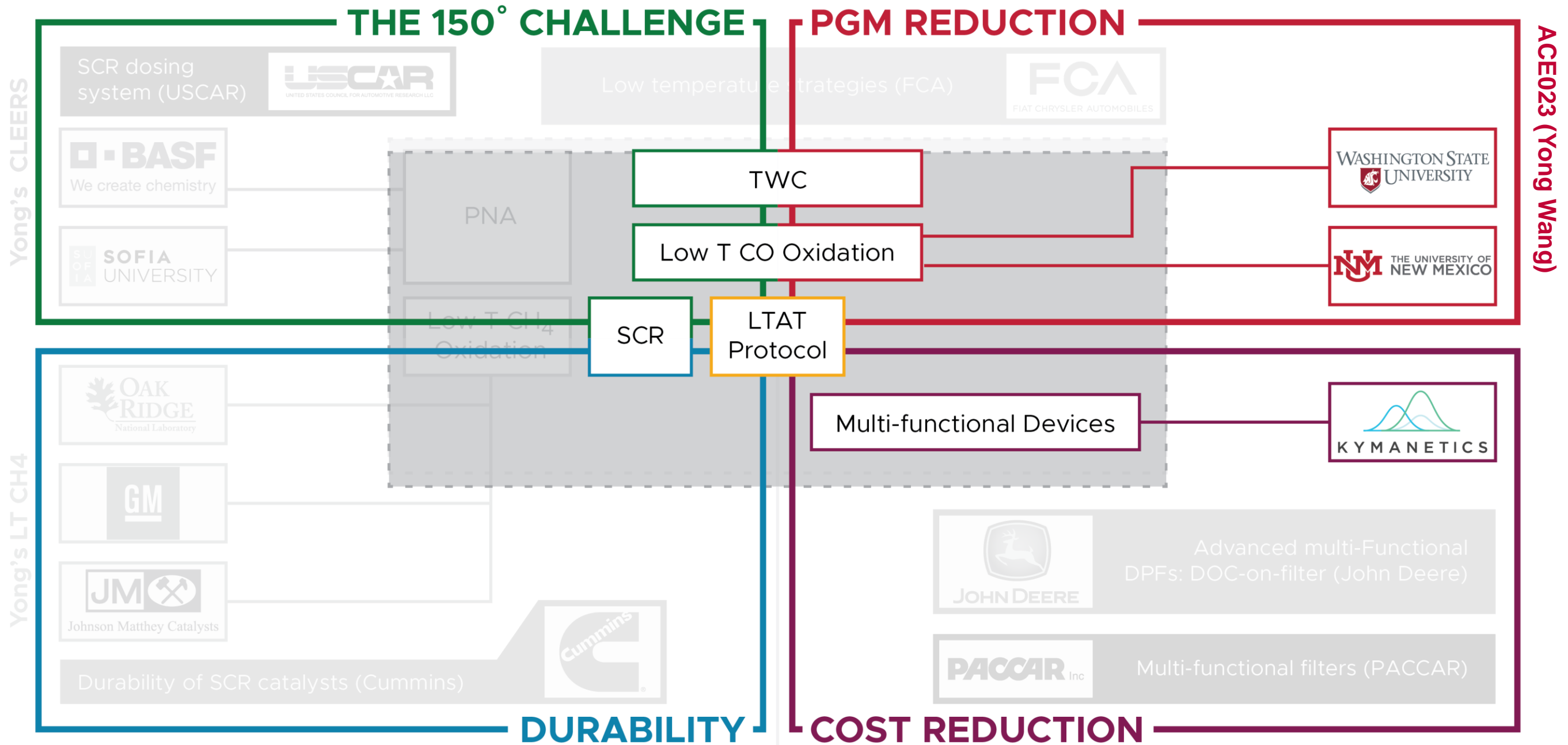


## PNNL Fundamental and CRADA Projects:

- 1) Address the 150°C Challenge, PGM Reduction, Durability, and Cost;
- 2) Aligns with Industrial Priorities - Exemplified by 5 AMR Presentations

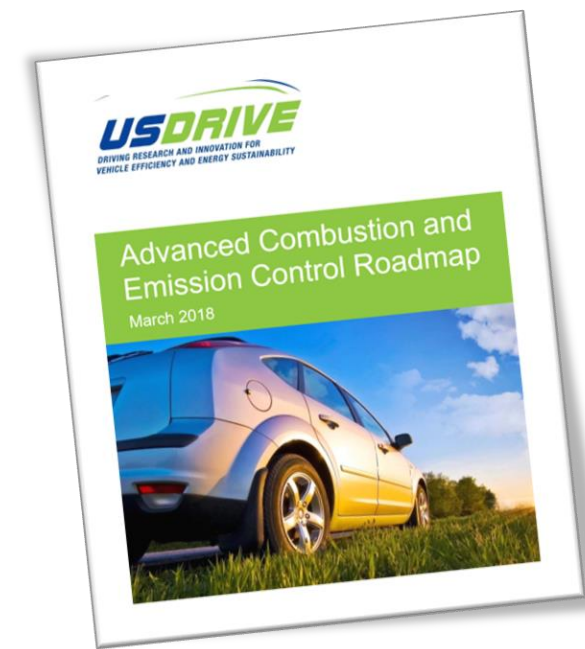


# Fundamental Tasks (SCR, TWC, LTAT, Multifunctional Devices) Focus on Four Important Areas and Align With Industrial Priorities





# Relevance



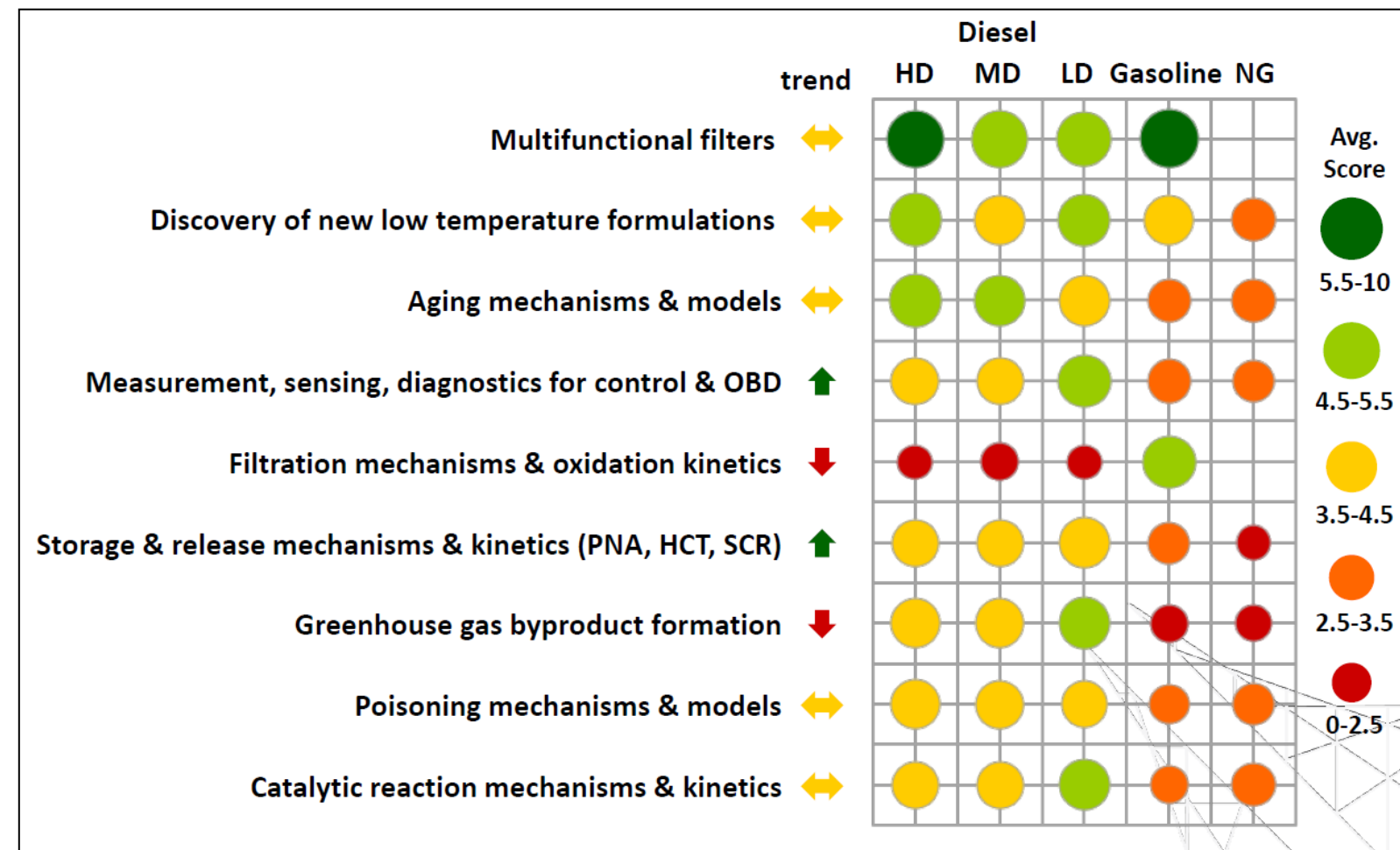
## 2018 Advanced Combustion and Emission Control Roadmap

- ▶ Increase internal combustion engine efficiency through advanced aftertreatment (driven by U.S. EPA Tier 3 Bin 30 emission standard).
- ▶ Achieve greater than 90% conversion of criteria pollutants (NO<sub>x</sub>, CO, HCs) at 150°C for the full useful life of the vehicle.\*
- ▶ Reduce the Platinum Group Metal (PGM) content to reduce commercial risk to PGM market volatility.
- ▶ Reduce cost, size, and complexity of emission control system with multifunction catalysts that combine multiple components onto one substrate.
- ▶ Develop models and simulation tools (molecular level to the system level) to predict performance and better understand catalytic processes.

## High Priority Research Areas (2019 Industrial Survey)

- ▶ Multifunctional filters
- ▶ Low temperature catalysts
- ▶ Aging

\*defined as the longer of 150,000 miles or 15 years



# Overview

## Timeline

- ▶ Status: On-going core R&D
- ▶ Particulate/filtration activity originated in FY03

## Budget

- ▶ FY20 funding: \$557K
  - SCR: \$300K
  - LTAT, TWC, etc: \$147K
  - M/F devices: \$110K

## Barriers

- ▶ Emission controls contribute to durability, cost and fuel penalties
  - Low-temp performance is now of particular concern
- ▶ Improvements limited by:
  - Available modeling tools
  - Chemistry fundamentals
  - Knowledge of material behavior
- ▶ Effective dissemination of information

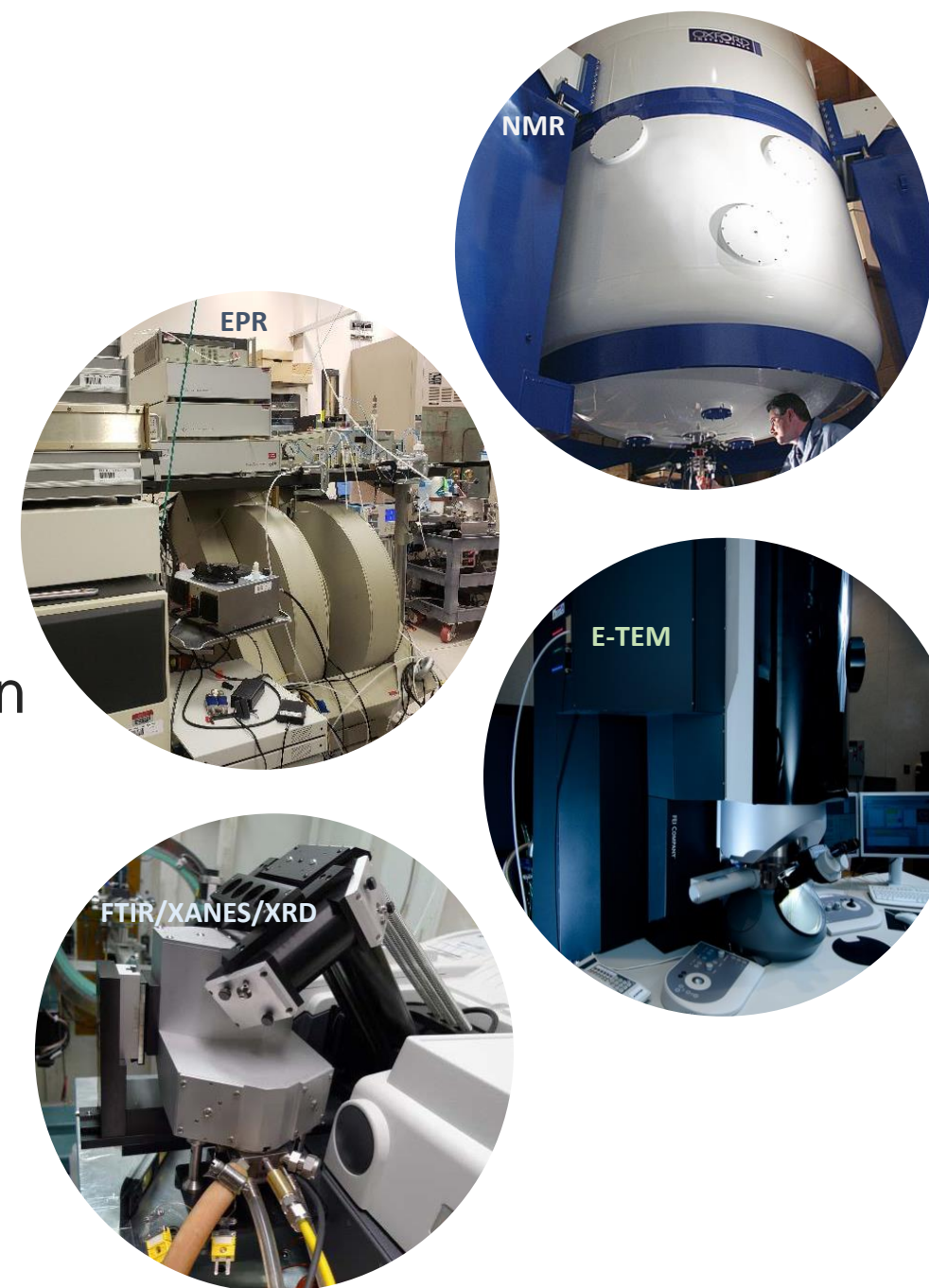
## Partners

- ▶ DOE Advanced Engine Crosscut Team
- ▶ CLEERS Focus Group
- ▶ 21CTP partners
- ▶ U.S. CAR/U.S. DRIVE ACEC team
- ▶ Oak Ridge National Lab
- ▶ Kymanetics, Inc.
- ▶ Cummins, JMC, FCA



## Approach/Strategy

- ▶ Build on PNNL's strong base in fundamental sciences to unravel the barriers needed to improve low temperature activity and high temperature durability:
  - Institute for Integrated Catalysis (IIC)
  - Environmental Molecular Sciences Laboratory (EMSL)
- ▶ Orient strongly towards applications and commercialization
  - OEMs
  - TIER 1 suppliers
- ▶ Work closely with our partners and sponsors
  - ORNL
  - DOE Advanced Engine Cross-Cut Team

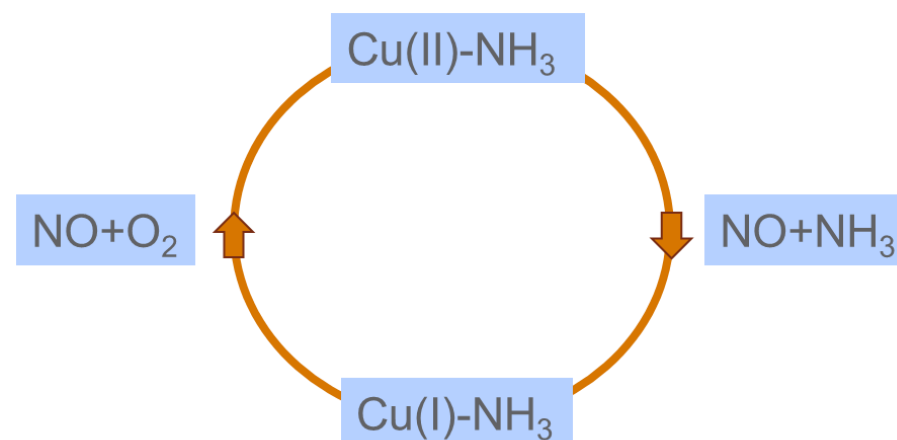
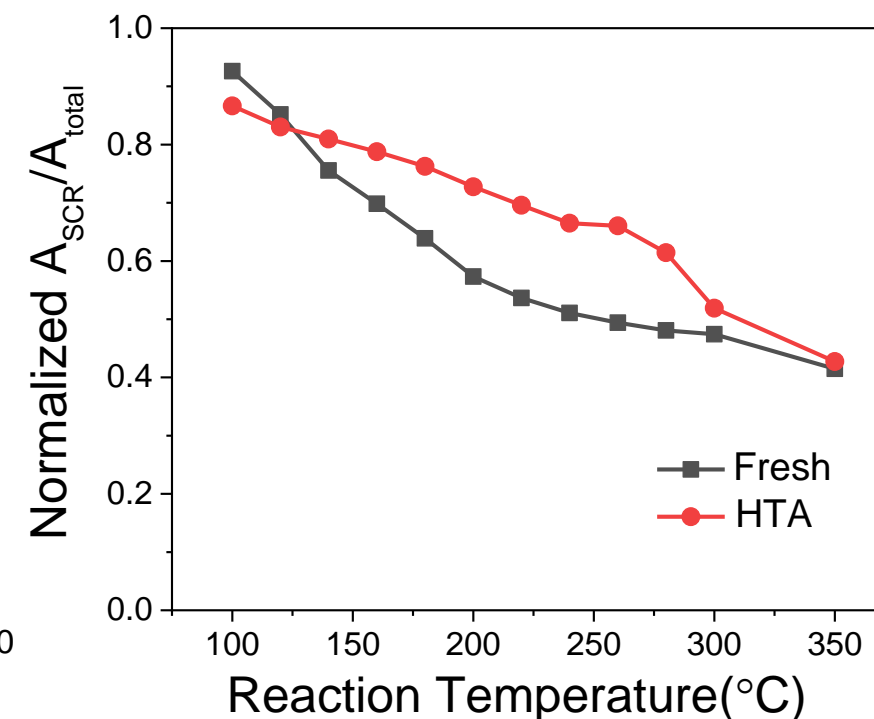
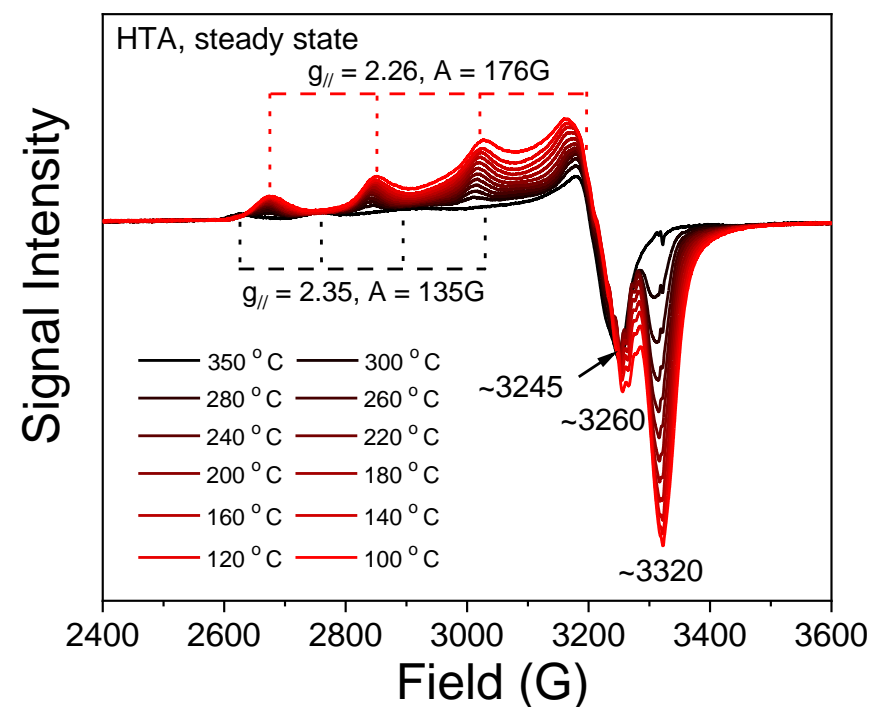
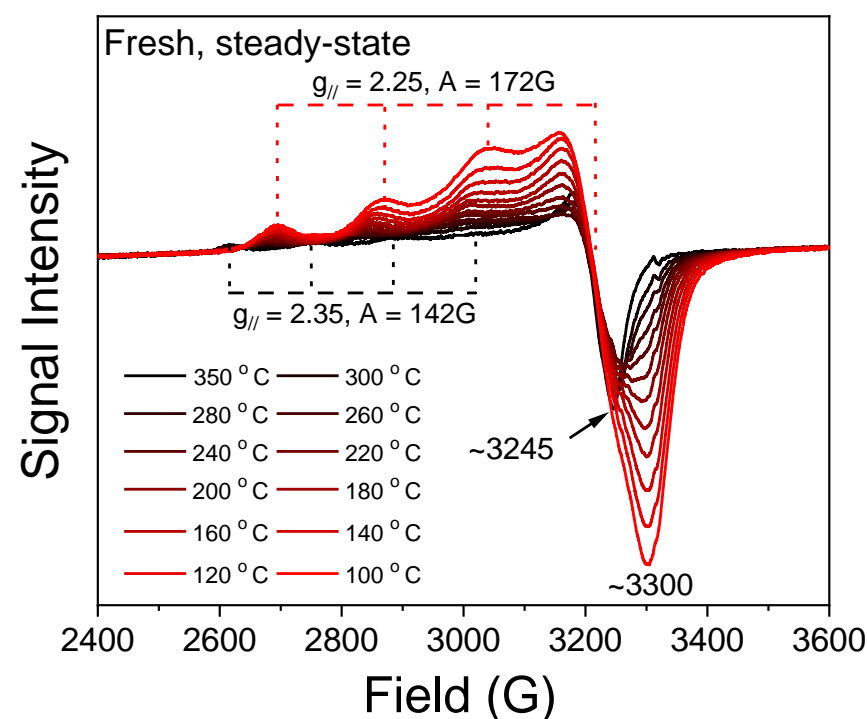


# Technical Milestones

Milestones	Date	Status
Establish in situ EPR to understand the site requirement, low temperature constraints, and degradation for SCR	3/31/2020	√
U.S. DRIVE Protocol test of leading candidate CO oxidation catalysts	6/30/2020	√
Complete initial studies of TWCs for stoichiometric combustion engines	9/30/2020	On track
Demonstrate operation of system for examination of axial conversion profiles (SPACI-MS or similar)	9/30/2020	On track



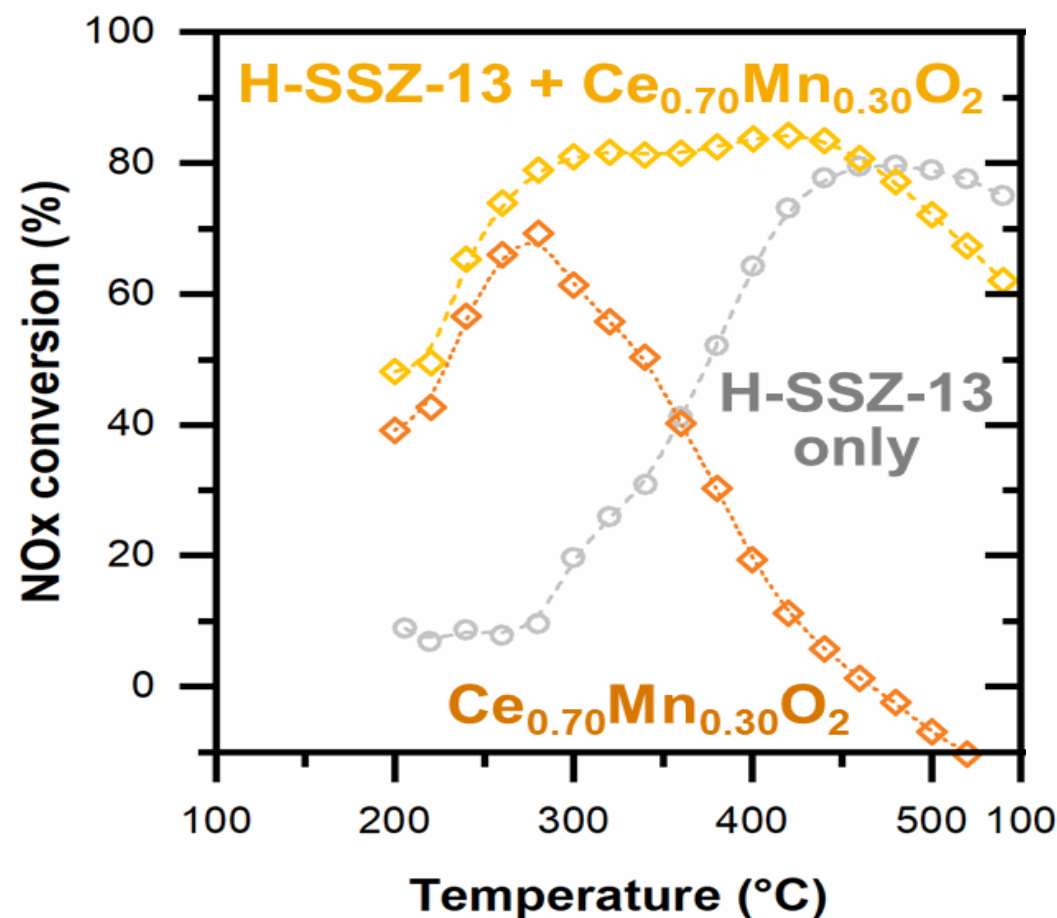
# Accomplishments (SCR) Hydrothermal Aging of Cu/SSZ-13 Leads to the Formation of More Stable and Less Active Cu(II)-NH<sub>3</sub> intermediates, Reducing SCR Activities



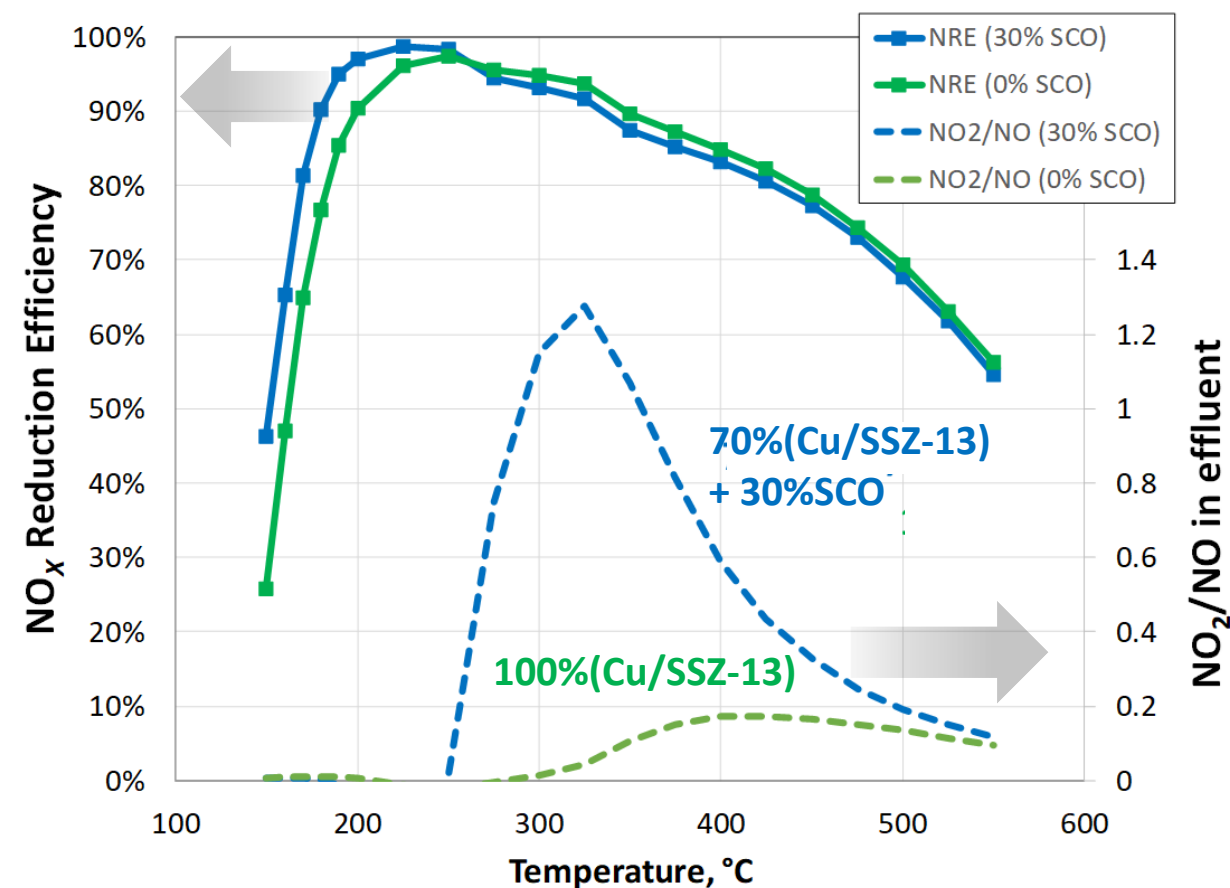
- ▶ *in situ* EPR capabilities recently developed allows the comparative studies between fresh and hydrothermally aged Cu/SSZ-13 catalysts under standard SCR conditions.
- ▶ EPR parameters (high-field positions, hyperfine tensors) reveals the conversion of Cu(II)-NH<sub>3</sub> to Cu(II)-O<sub>L</sub> intermediates as temperature rises.



# Accomplishments (SCR) The Presence of MnCe Oxides Synergistically Increases Low-Temperature SCR Activity



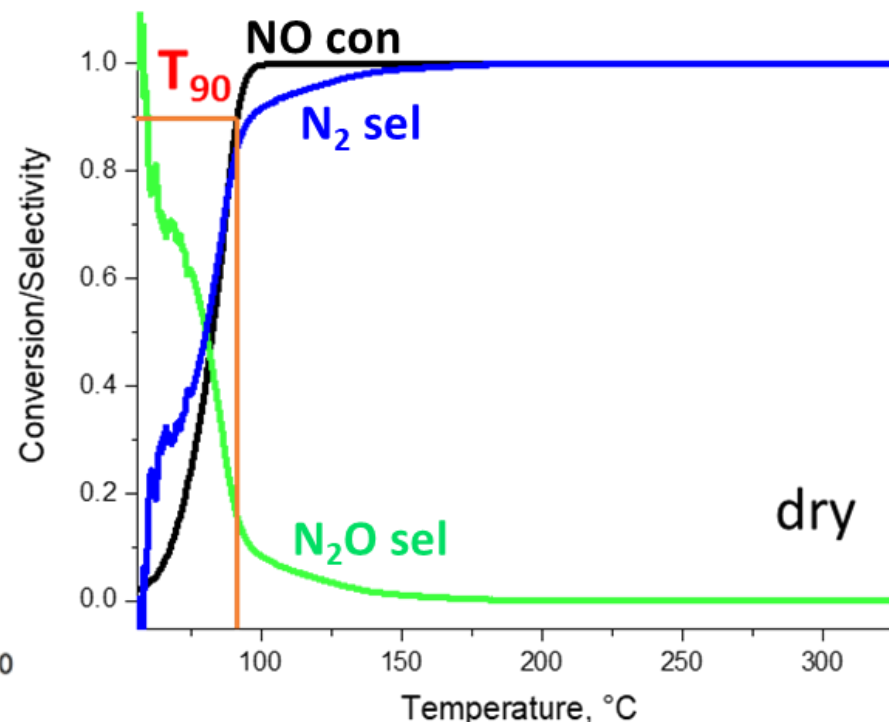
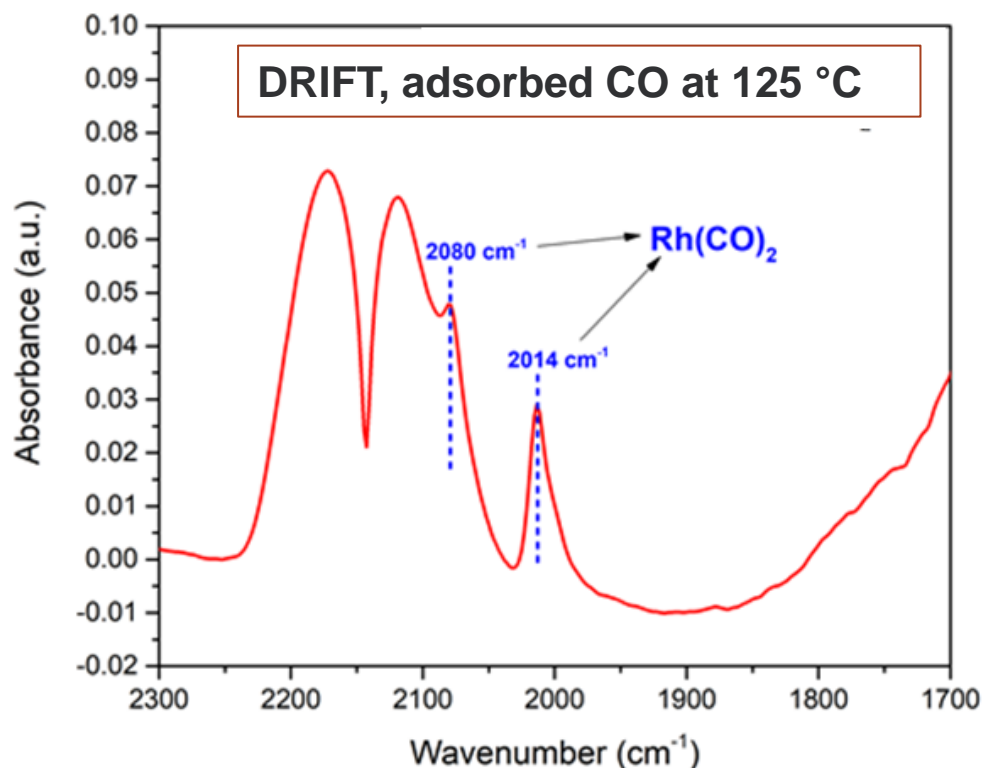
175 ppm NO, 175 ppm NO<sub>2</sub>, 350 ppm NH<sub>3</sub>, 15% O<sub>2</sub>, 6% H<sub>2</sub>O, 8% CO<sub>2</sub> (balanced N<sub>2</sub>), 150 mg catalyst, SV = 400 L g<sup>-1</sup> h<sup>-1</sup>



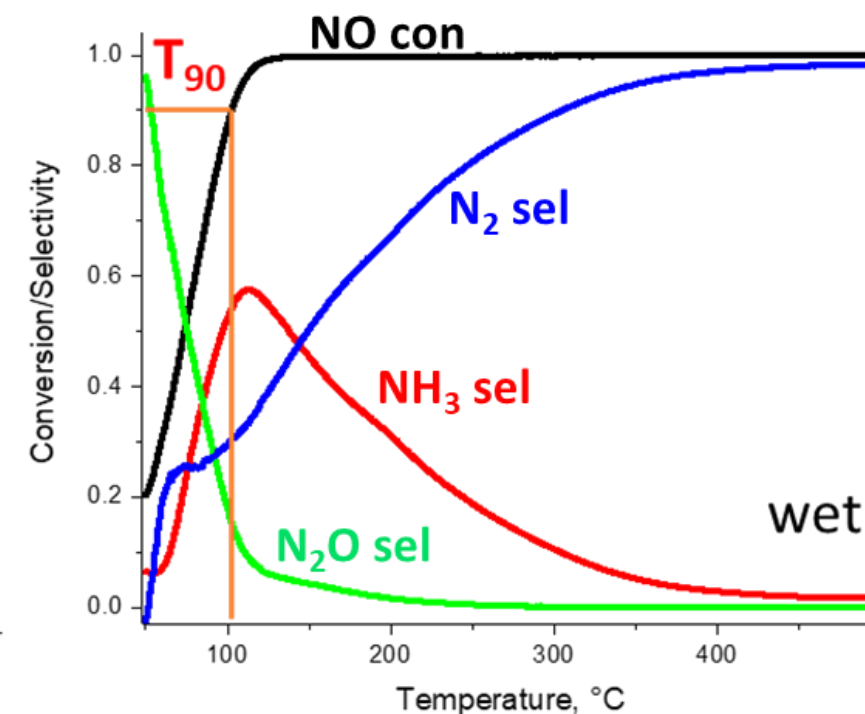
300 ppm NO, 350 ppm NH<sub>3</sub>, 10% O<sub>2</sub>, 6% H<sub>2</sub>O, 8% CO<sub>2</sub> balance of N<sub>2</sub>, SV=35,000 h<sup>-1</sup>, ~70 g/L active phase

- ▶ NO<sub>2</sub> SCR reaction pathways facilitated by SCO phase, increasing low temperature SCR activity.
- ▶ No adverse impact of NH<sub>3</sub> oxidation at elevated temperature

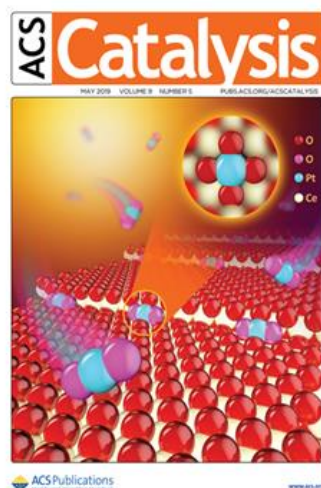
# 0.1wt% Rh/CeO<sub>2</sub> Single Atom Catalyst Is Highly Active for NO Reduction



120mg cat., 460 ppm NO, 1750 ppm CO,  
balanced with N<sub>2</sub>, 150,000 mL·g<sub>cat</sub><sup>-1</sup>·h<sup>-1</sup>



120mg cat., 460 ppm NO, 1750 ppm CO, 2.6%  
H<sub>2</sub>O, balanced with N<sub>2</sub>, 150,000 mL·g<sub>cat</sub><sup>-1</sup>·h<sup>-1</sup>

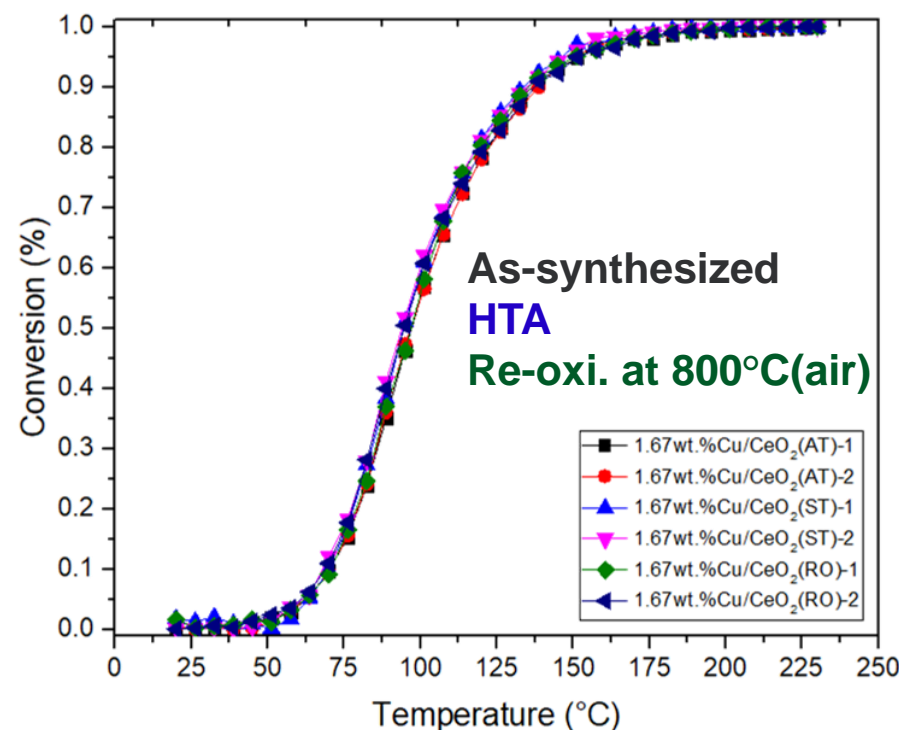


- ▶ Thermally durable 0.1%Rh/CeO<sub>2</sub> single atom catalyst was synthesized using atom trapping (800°C in air).
- ▶ IR confirms all the Rh ions are located in a structurally identical position and are stable even in CO at 125°C.
- ▶ Remarkably high NO reduction activities were observed under both dry and wet conditions, with T<sub>90</sub> of ~85 and ~100°C, respectively.

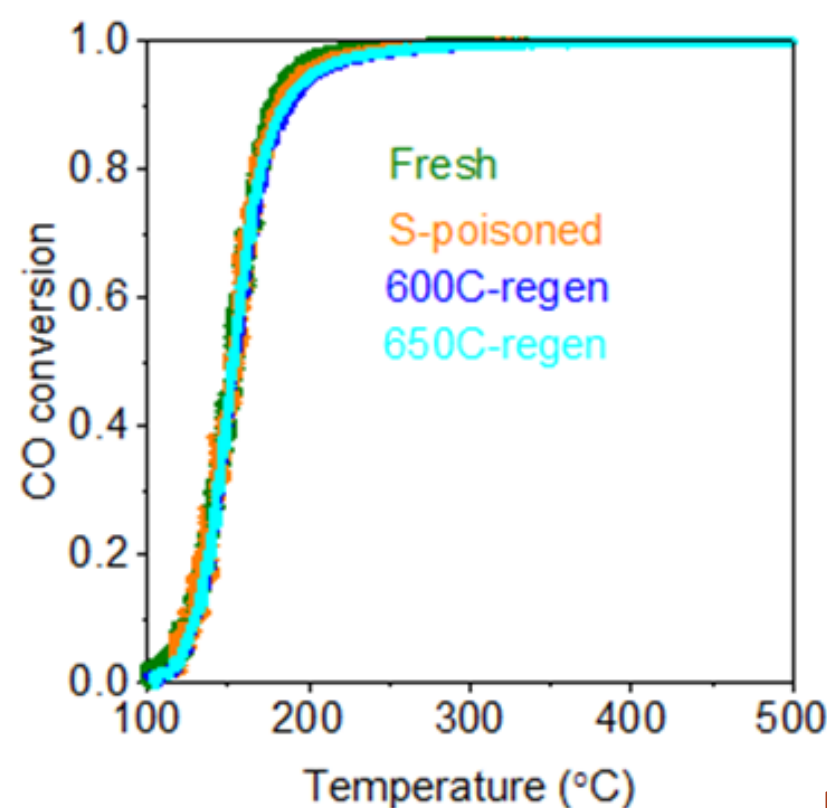


## Accomplishments (CO Oxidation)

# 1.67wt% Cu/CeO<sub>2</sub> Single Atom Catalyst Is Highly Active and Durable for CO Oxidation



1%CO, 4%O<sub>2</sub> balanced with Ar.  
300,000 mL·g<sub>cat</sub><sup>-1</sup>·h<sup>-1</sup>, 20mg catalyst.



**Fresh**  
De-greening: 700°C,  
4h, 10% O<sub>2</sub>, 5% H<sub>2</sub>O,  
200L g<sup>-1</sup> h<sup>-1</sup>.

**S-poisoned**  
Sulfur exposure: 300°C,  
100min, 5 ppm SO<sub>2</sub>, 12%  
O<sub>2</sub>, 6% H<sub>2</sub>O, 200L g<sup>-1</sup> h<sup>-1</sup>.

**600C-regen**  
Pretreatment: 600°C,  
20min, 12% O<sub>2</sub>, 6% H<sub>2</sub>O,  
6% CO<sub>2</sub>, 200L g<sup>-1</sup> h<sup>-1</sup>.

**650C-regen**  
Pretreatment: 650°C,  
20min, 12% O<sub>2</sub>, 6% H<sub>2</sub>O,  
6% CO<sub>2</sub>, 200L g<sup>-1</sup> h<sup>-1</sup>.

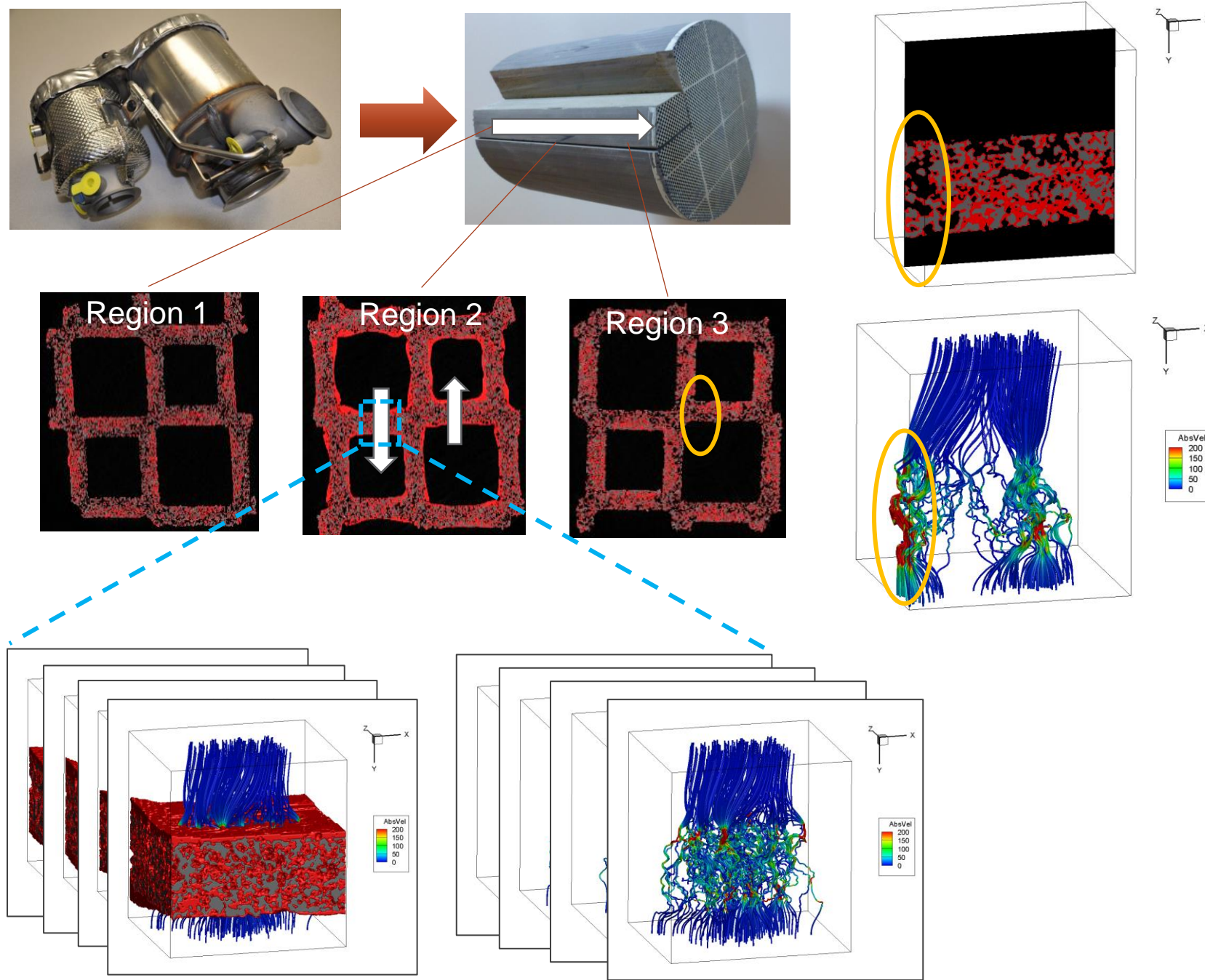
U.S.DRIVE Protocols

- ▶ Thermally durable 1.67wt%Cu/CeO<sub>2</sub> single atom catalyst was synthesized using atom trapping (800°C in air).
- ▶ T<sub>90</sub>~85°C maintained: as-synthesized, HTA (10% H<sub>2</sub>O in air for 9 h at 750°C), oxidative treatment (800°C in air for 16 h) followed by HTA – confirmed by two replicated experiments.
- ▶ No deactivation after sulfur exposure following the U.S.DRIVE protocols.

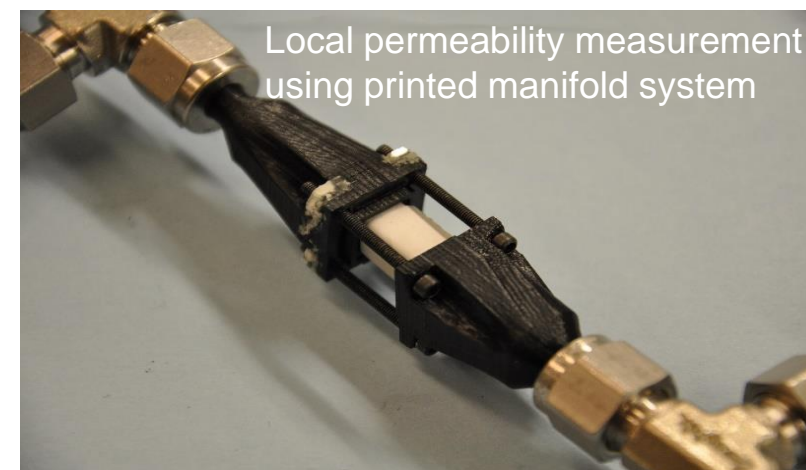


## Accomplishments (Multi-functional Device)

# Pore Scale Flow Simulated on a Commercial SCR Filter



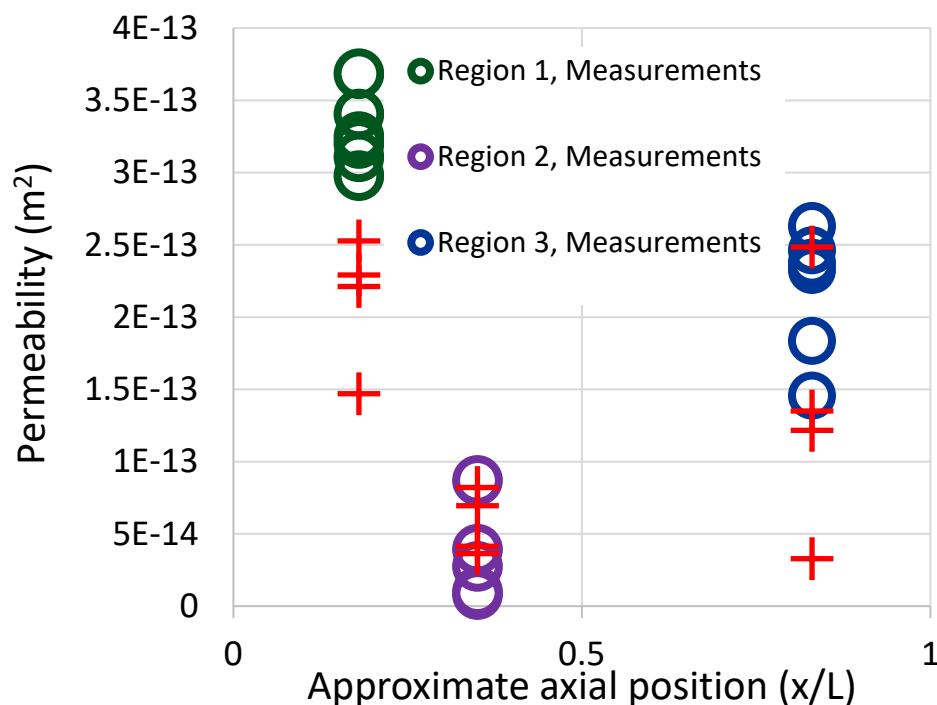
- ▶ Micro X-Ray CT data from three distinct axial coating regions in a commercial SCR-filter allowed reconstructions for a series of computationally demanding pore-scale flow simulations using HPC resources at PNNL.
- ▶ Effects of microstructure on the flow are predicted – major flow pathways through relatively open regions in wall.
- ▶ Predicted permeability can be validated by measured axial variations in filter permeability using small samples.



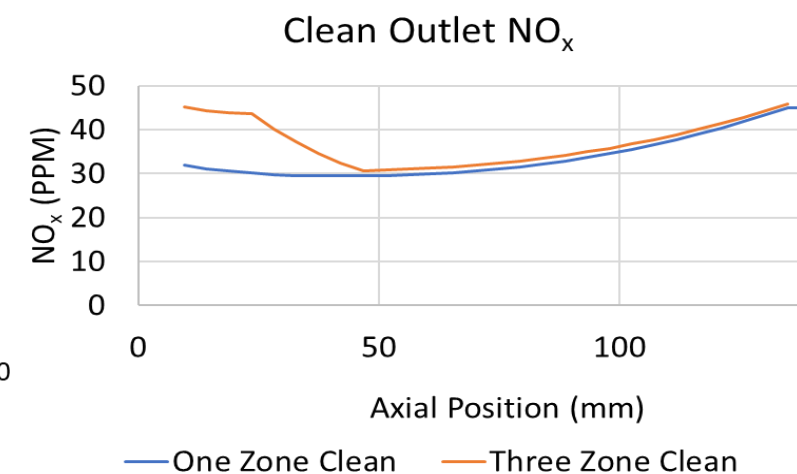
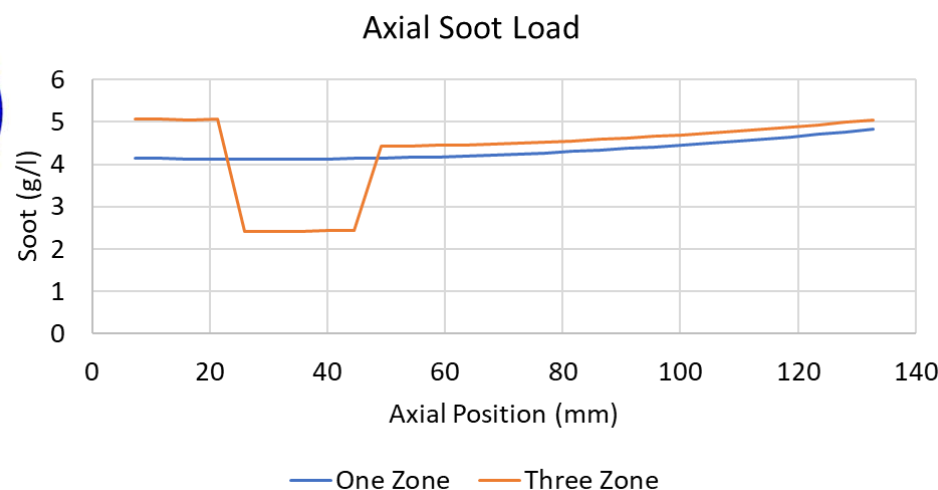
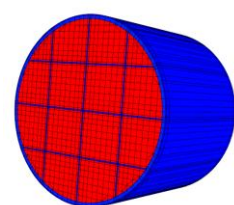
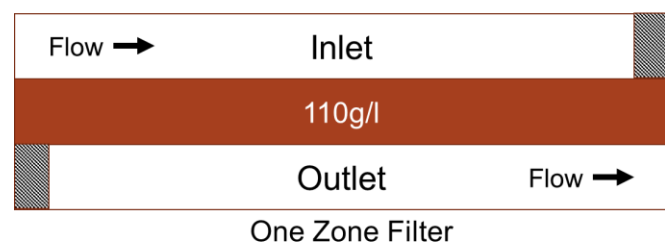
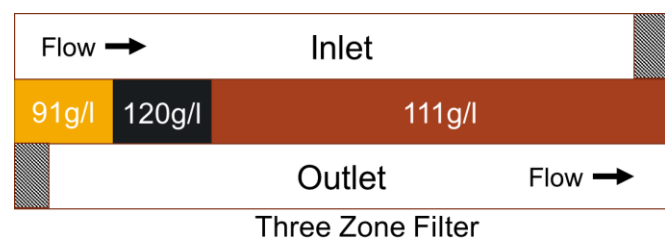


## Accomplishments (Multi-functional Device)

# Device-scale Modeling Predicts Soot Loading and NO<sub>x</sub> Conversion

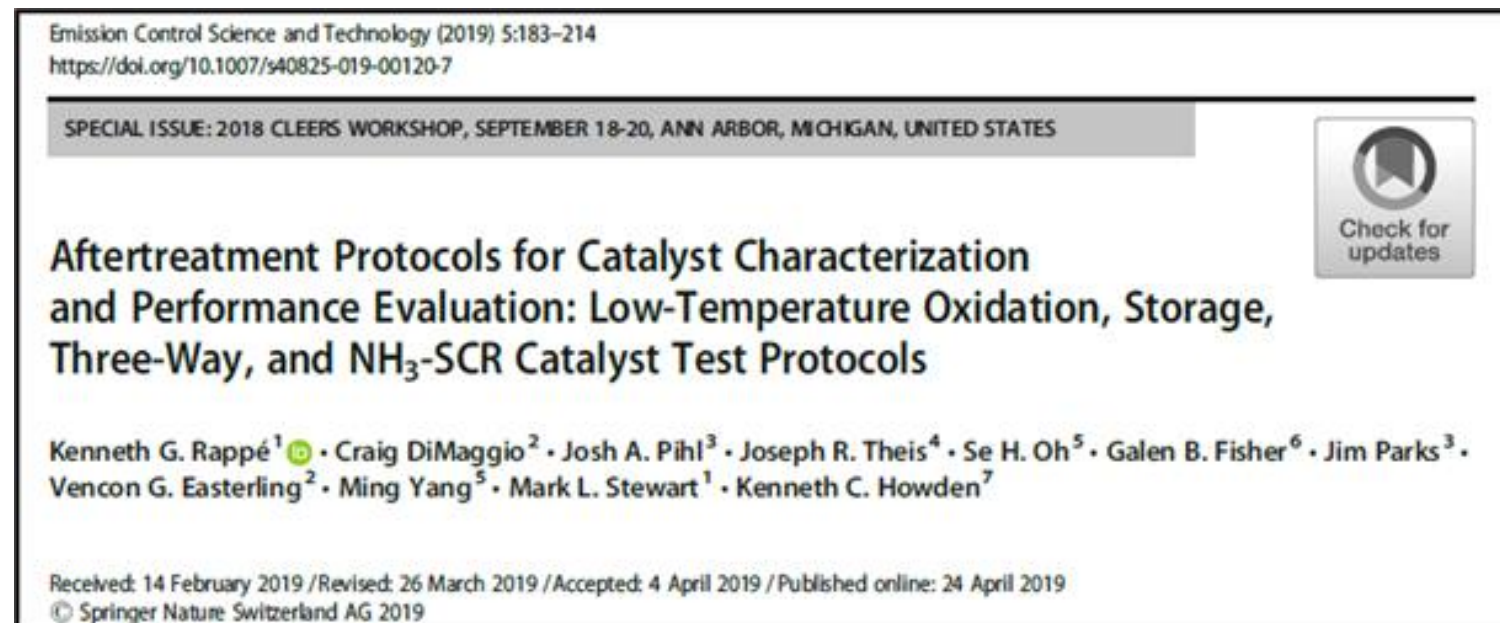


- ▶ Lattice-Boltzmann simulations show same trend as test data: significantly lower permeability in heavily coated Region 2 and higher permeability in lightly coated Region 1
- ▶ Device-scale models created with measured local permeabilities can be used for comparison with other devices, e.g., similar overall catalyst loading distributed uniformly:
  - Models suggest that axial coating distribution did not appear to significantly impact overall backpressure or NO<sub>x</sub> conversion for the design and conditions examined



# Low-Temperature Catalyst Test Protocols & PGM Utilization

- ▶ Open literature release of all four low-temperature catalyst test protocols
  - Oxidation, Storage, TWC, SCR
- ▶ Planning and road-mapping efforts regarding the need to lower catalyst PGM usage in emission control
  - Presentations given to the ACEC Tech Team and the APTLC
  - Planning efforts have, in part, led to the issuance of DOE-EERE FOA DE-FOA-0002197
- ▶ On-going interaction with the ACEC tech team and the LTAT sub-group
  - Bi-monthly ACEC and AE Crosscut participation
  - Bi-weekly LTAT sub-group participation
  - Prioritization of activities moving forward
- ▶ Organized & moderated 2019 CLEERS workshop panel discussion





# Responses to Previous Year Reviewers' Comments

## Reviewers' Comments

## PNNL Responses

PNNL team has several external collaborators, but no external partners

This core program provides fundamental understanding of broad interest to industry. Individual CRADA projects build from core work.

Should also consider strategies for managing CO and hydrocarbon emissions at low temperature

CO oxidation is actively studied. HC oxidation is part of the U.S.DRIVE protocol studies.

How to make nitrogen dioxide (NO<sub>2</sub>) at low temperatures

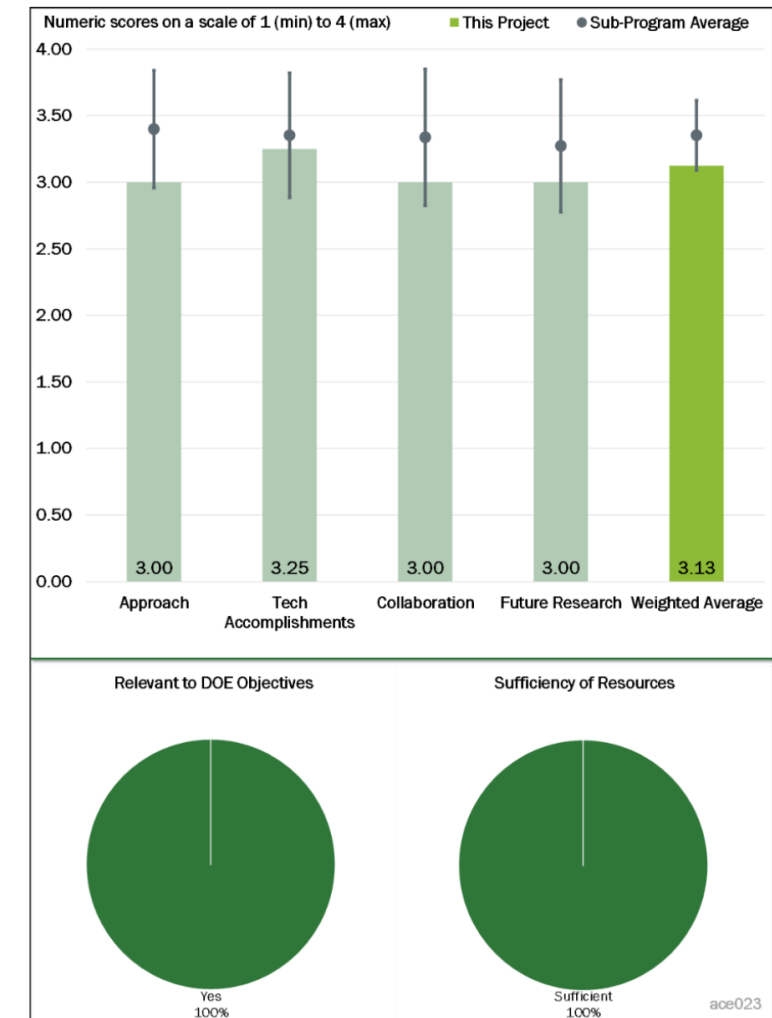
Integration of SCR with metal oxides is part of work.

Why not continue Na-co cation to increase the activity of Cu/SSZ-13?

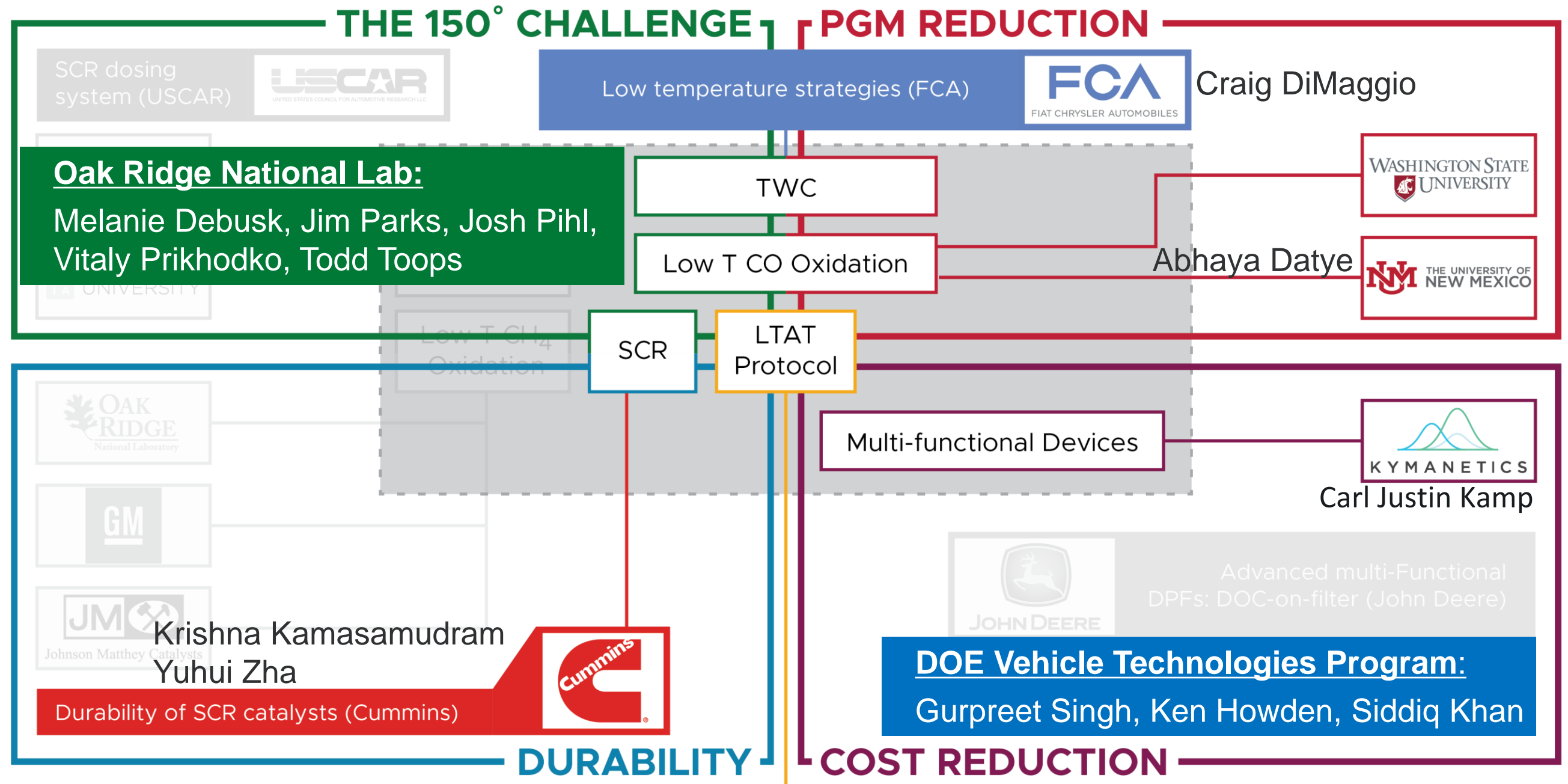
As detailed in our recent publication (*Catal. Today*, **2019**, 339,233-240), Na<sup>+</sup> competes with Cu site, limiting the improvement of SCR activity.

Need to develop detailed SCR-DPF and TWC-GPF system models

Currently working to incorporate learnings from our fundamental program into device and system scale models using commercial software including Axisuite by Exothermia



# Collaboration and Coordination with Other Institutions





## Remaining Challenges and Barriers

- ▶ Linking learning from lab accelerated model materials with field-aged commercial catalysts.
  - Distinguishing thermal degradation, hydrothermal degradation and chemical degradation for examining aged (used) catalysts, and identification of representative descriptor for aging from such complexity.
- ▶ Translating efficiency gains of single atom catalysts prepared by atom trapping to production scale while ensuring Bin30/SULEV30 emissions compliance.
- ▶ Understanding more completely the effects of coating distribution in multi-functional filters employing a range of advanced substrates and coating processes is needed for optimization of next-generation devices.
  - Understanding the relationship between filter wall surface texture and pressure drop response during loading is lacking.

# Proposed Future Work

## SCR

- ▶ Study the mechanisms for the oxide promoted low temperature NO<sub>x</sub> conversion to enable the development of zeolite + oxide hybrid SCR catalysts, and understand how these two phases influence each other's long-term stability.
- ▶ Develop new spectroscopic methods for examining aged and on-road catalysts, and develop correlations between mileage and catalyst performance.

## TWC

- ▶ Evaluate HC oxidation, S poisoning, and further reduction of Rh content of Rh single atoms prepared by atom trapping.

## Multi-functional devices

- ▶ Analyze catalyst distribution in new SCR-Filter system deployed in the U.S. in 2020.
- ▶ Conduct fundamental filtration experiments to understand effects of porosity variation across the thickness of ceramic exhaust filter walls.

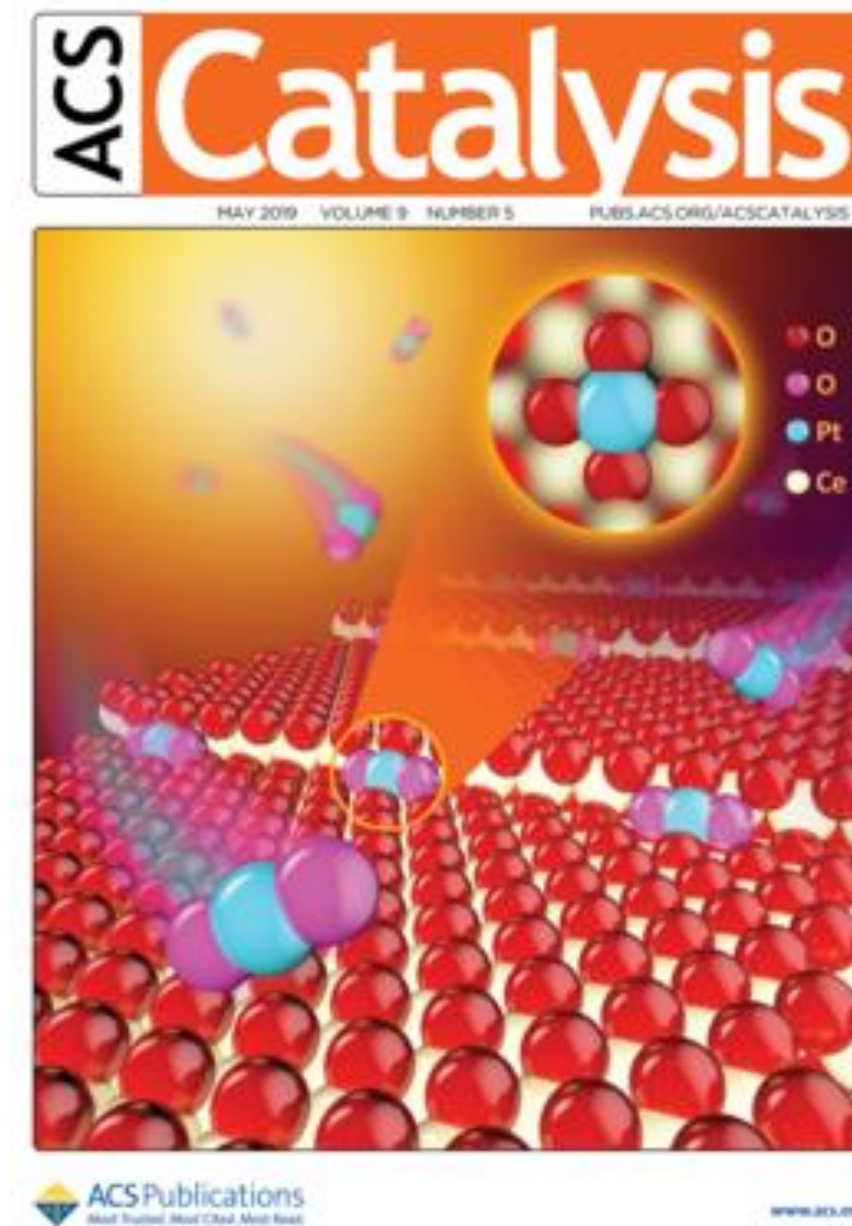
## LTAT

- ▶ Continue PGM road-mapping efforts, e.g., PGM review article with ORNL, early planning of PGM workshop (targeting 2021).
- ▶ BES – Catalysis Science engagement RE: PGM fundamental science.



## Summary

- ▶ Pulsed 2-dimensional *in situ* electron paramagnetic resonance (EPR) provides unprecedented insight on Cu/SSZ-13 catalyst deactivation under full useful life aging.
- ▶ SCR activities are enhanced by the presence of SCO phase, e.g., MnCe oxides, providing a means to improve low temperature SCR activity.
- ▶ Thermally durable single atom Cu and Rh catalysts prepared by atom trapping exhibit high activity in CO oxidation and NO reduction, contributing to PGM reduction and catalyst cost savings.
- ▶ Pore scale flow simulations of a commercial SCR-filter can connect its microstructure to its macroscopic behavior.
- ▶ On-going interaction with LTAT sub-group of the ACEC Tech Team provides guidance on prioritizing future activities.







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# Thank you





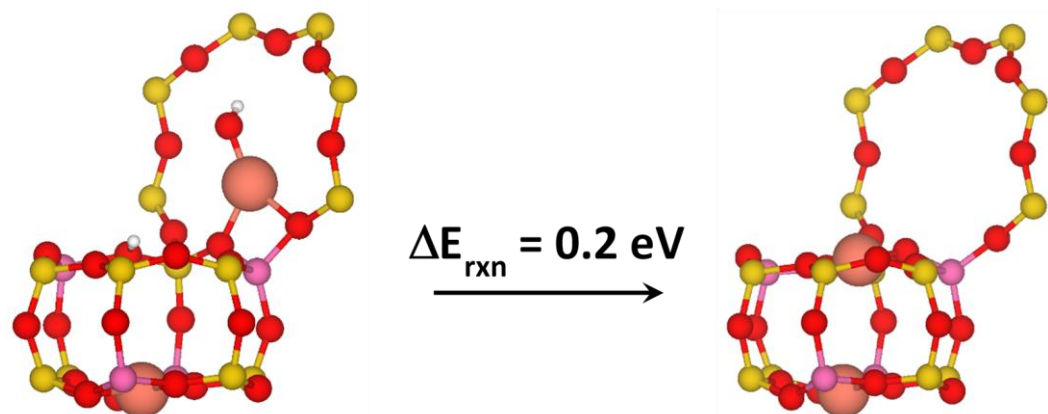
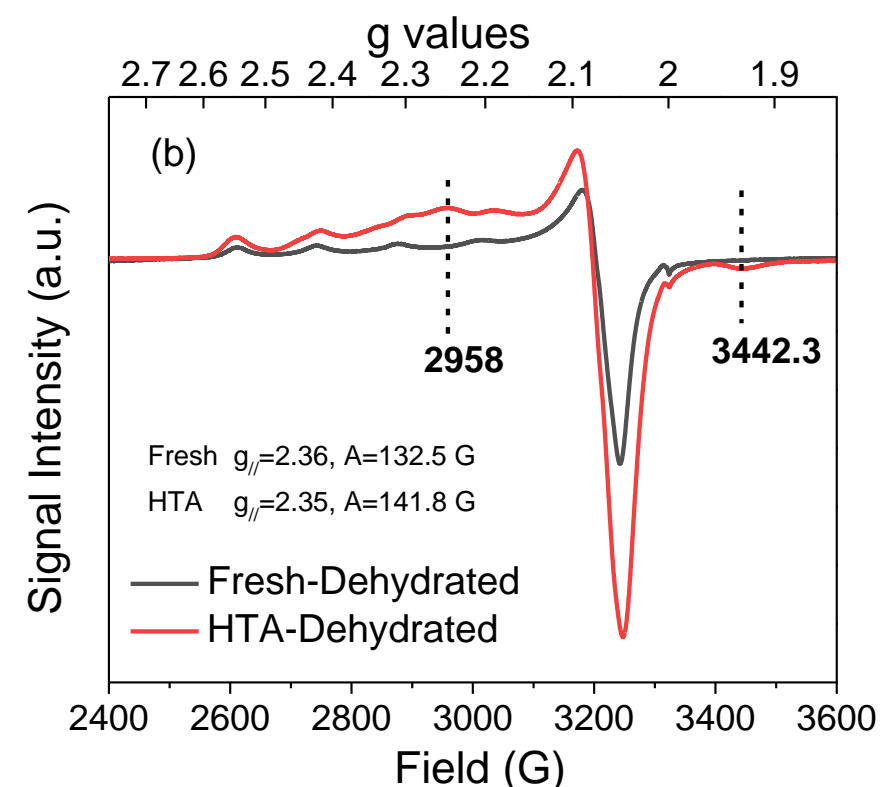
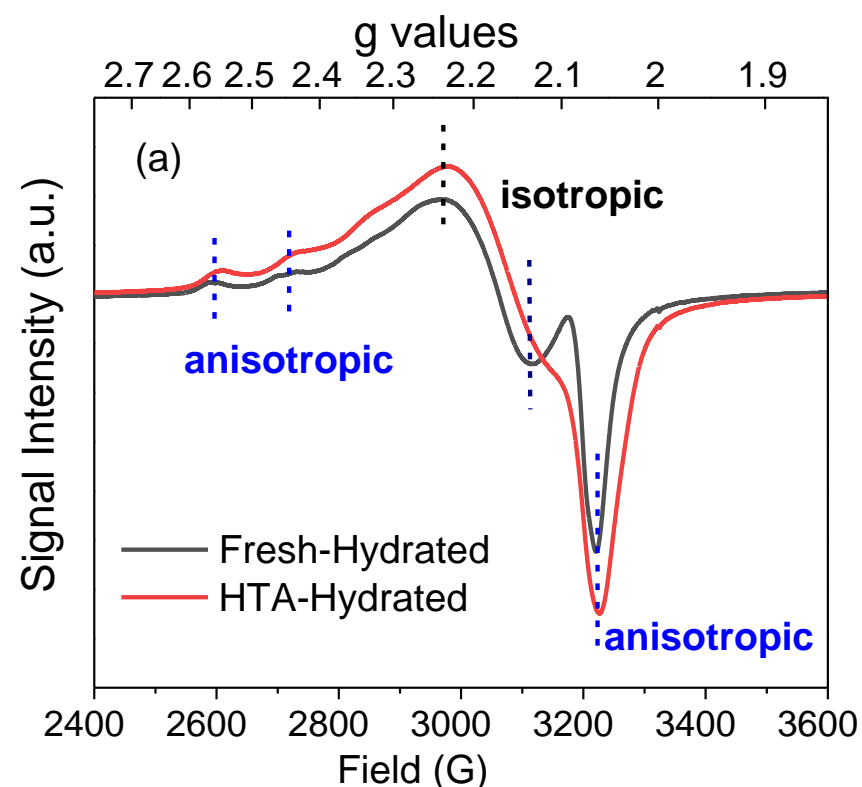
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# Technical Backup Slides



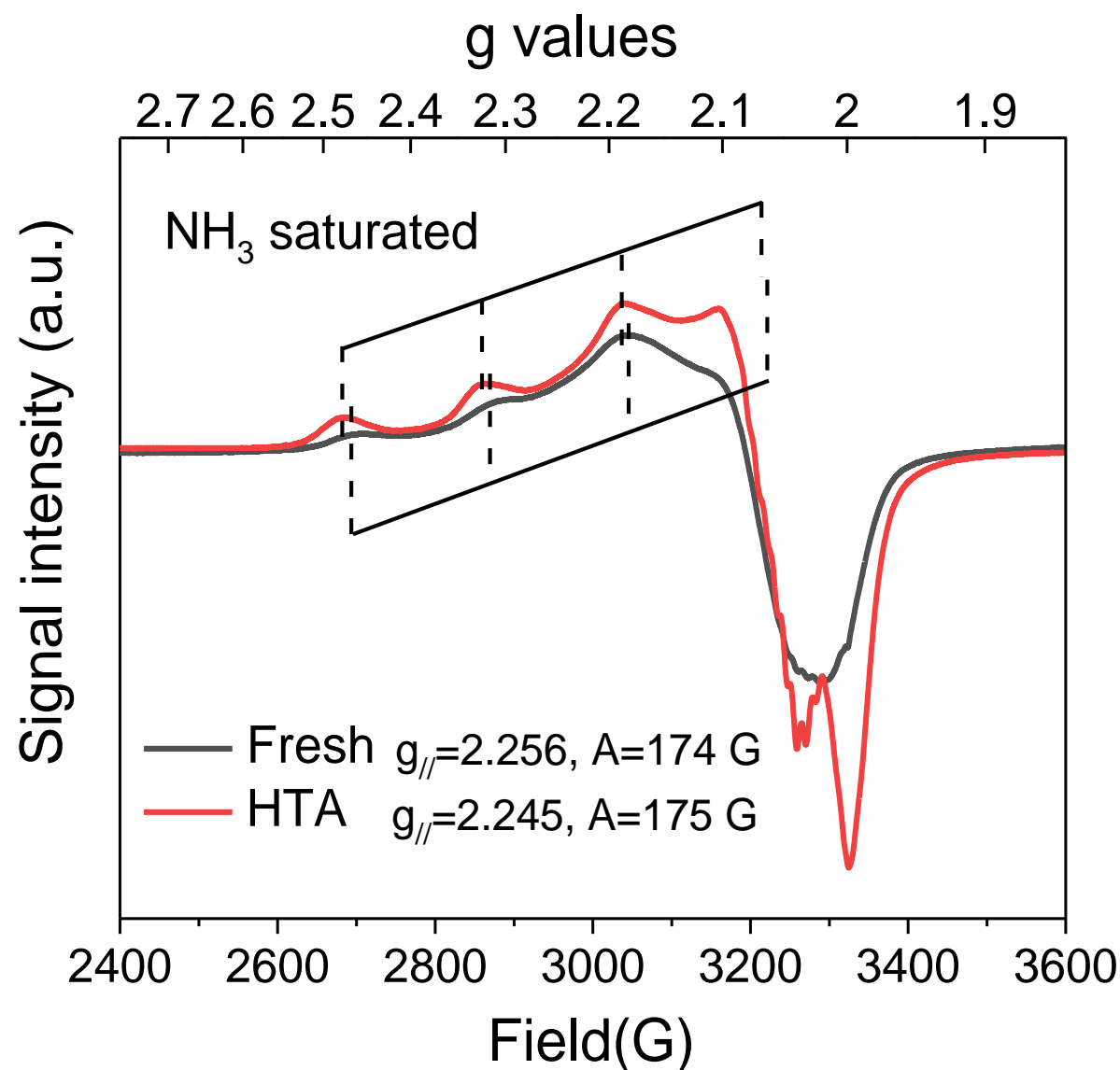
# Ex situ EPR Identifies Isolated Cu(II) Pair In Double 6MR of SSZ-13



- ▶ EPR studies were conducted on hydrated and dehydrated fresh and HTA Cu/SSZ-13.
- ▶ Hydrothermal aging causes stronger Cu-support interactions as evidenced by the increased anisotropy of Cu(II) sites.
- ▶ One of the mechanisms for the increased Cu-support interaction is the conversion of  $\text{ZCuOH}$  to  $\text{Z}_2\text{Cu}$ , which leads to the formation of isolated Cu(II) pair in double 6MR prism. Such species display unique EPR signals.
- ▶ More subtle Cu relocations also increase Cu-support interactions.



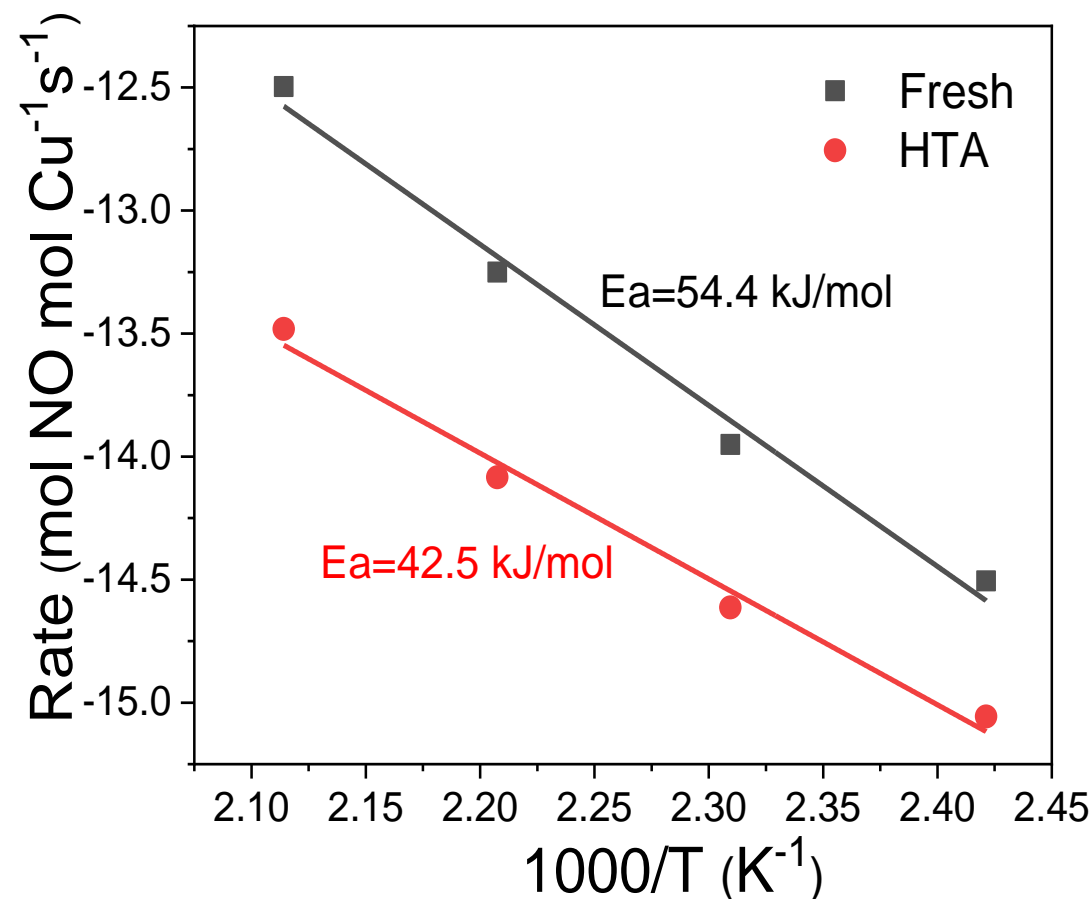
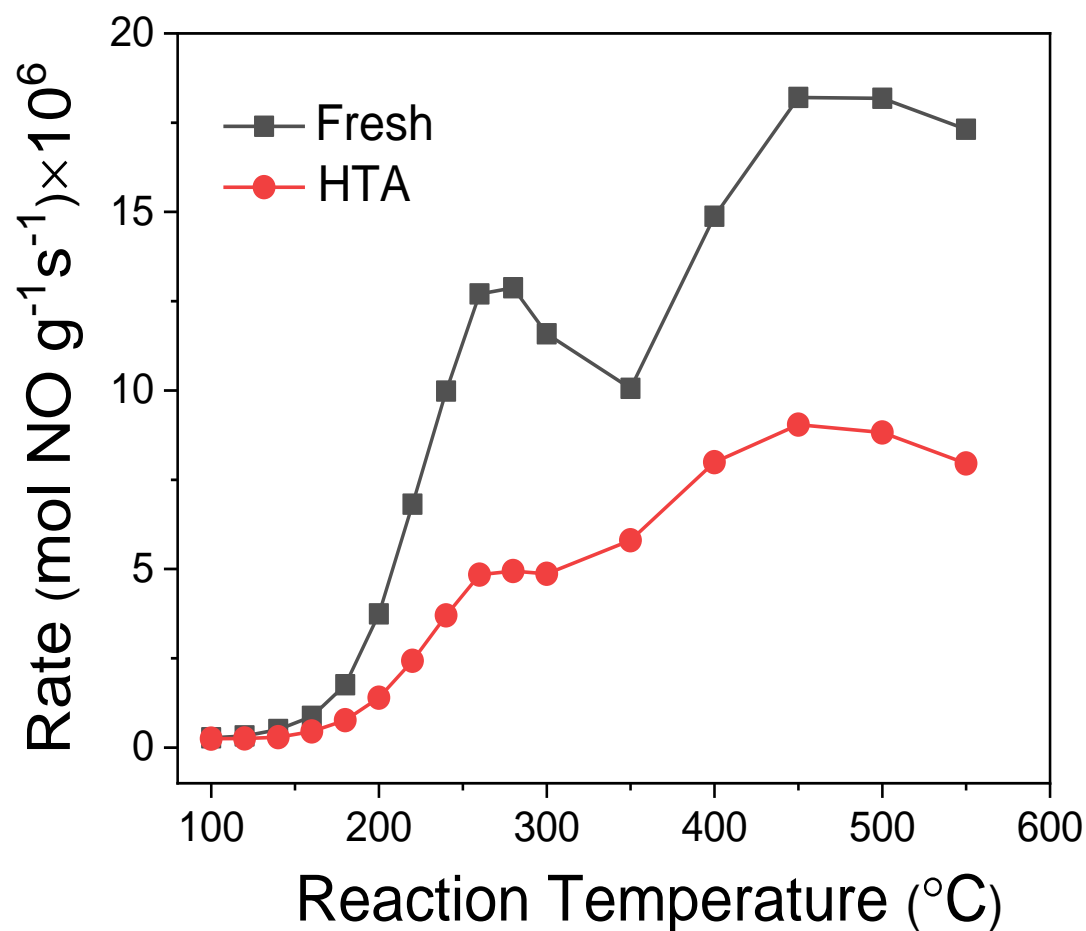
# *ex situ* EPR on NH<sub>3</sub>-Saturated Cu/SSZ-13 (Fresh and HTA) Unravels the Cu-Support Interactions



HTA sample contains more Cu ions with less variability of structure than the fresh catalyst, causing the highest field hyperfine line to overlap the  $g_{\perp}$  region.

in the HTA spectra, superhyperfine from <sup>14</sup>N is clearly visible, again due to stronger Cu-support interactions of the HTA sample.

# Steady-state Standard SCR Tests Show Up to 60% Activity Loss by HTA



- ▶ In the absence of support structure degradation or loss of active sites, Cu relocations along during hydrothermal aging (some of them are even very minor) profoundly affect SCR performance.
- ▶ Increased Cu-support interactions make Cu less active (i.e., less efficient Cu-reactant interactions) by as much as ~60% under differential conditions.



# Organized & Moderated 2019 CLEERS Workshop Panel Discussion

2019 Topic – PGM utilization and replacement in aftertreatment

- ▶ Organized by PNNL, co-moderated by Ken Rappé (PNNL) & Craig DiMaggio (FCA)
- ▶ Panel participants
  - Christine Lambert, Ford
    - Topic introduction, emissions legislation
    - State of technology, current aftertreatment challenges
    - PGM: urgency in making less more effective, availability, (global) market direction, market volatility
  - Wei Li, GM
    - PGM challenge: aging (thermal, low-temperature activity, chemical), which drives loading
    - Near term (~2025) – gasoline (TWC) focused on PGM stability & doing more with less
    - Long term (10+ yrs) – reduce/replace PGM across all engine platforms
  - Tom Pauly, Umicore
    - Replacing PGM: alternative approaches, challenges presented to PGM alternatives
    - Strategies, needs from academia
  - Xinyi Wei, BASF
    - Diesel – unique challenges (e.g., low-temperature aging), making PGM more efficient
    - ULE regulations putting high demand on high performance; suppliers must engage academia now for 5-10 yr. impact on PGM usage
    - PNAs: must be justified, net benefit towards achieving regulatory targets with reduced overall PGM
  - Mario Castagnola, JM
    - JM's Global Modelling Manager, former Sr. Technical Program Manager for heavy-duty diesel
- ▶ Most presentations available on the CLEERS website: <https://cleers.org/event/2019-cleers-workshop/>